

FIELD PROCEDURE 18
Gaseous Organic Compounds
(Gas Chromatography)

Note: This procedure attempts to analyze about 90% of the total gaseous organics emitted from an industrial source and does not identify and measure trace amounts of organic compounds, such as those found in building air and fugitive emission sources. This procedure will not determine compounds that (1) are polymeric (high molecular weight), (2) can polymerize before analysis, or (3) have very low vapor pressures at stack or instrument conditions.

The forms in this section contain the information required by the test method; we are aware that some of the technology specified in the test method is obsolete. In these cases, the user should modify the forms to make them consistent with the technology used.

A. Pretest Survey and Pretest Survey Sampling

1. Obtain (from pretest surveys, literature surveys, experience, discussions with plant personnel, etc.) all information necessary to design the emission test, e.g., see FDS 18.
2. Obtain pretest survey samples of the gas and analyze to confirm the identity and approximate concentrations of the specific compounds. The following sections include suggested sampling procedures.

B. Glass Sampling Flasks

1. **Cleaning Procedure.** Clean a 250-mL double-ended glass sampling flask with Teflon stopcocks, without grease, as follows:
 - a. Remove the stopcocks from both ends of the flasks, and wipe the parts to remove any grease. Clean the stopcocks, barrels, and receivers with methylene dichloride. Clean all glass ports with a soap solution, then rinse with tap and deionized distilled water.
 - b. Place the flask in a cool glass annealing furnace, and heat up to 500°C and maintain at 500°C for 1 hr. Then shut off and open the furnace to allow the flask to cool.
 - c. Reassemble the flask. Purge the assembly with high-purity N₂ for 2 to 5 min. Close off the stopcocks after purging to maintain a slight positive N₂ pressure. Secure the stopcocks with tape.
2. **Evacuated Flask Procedure.** Use this procedure or the purged flask procedure (section B3) to collect the samples. At this time, the EPA does not approve using SUMMA[®] canisters for collecting Method 18 samples.
 - a. Evacuate the flask to the capacity of a high-vacuum pump; then close off the stopcock leading to the pump.
- b. Attach a 6-mm OD glass tee to the flask inlet with a short piece of Teflon tubing.
- c. Select a 6-mm OD borosilicate sampling probe of sufficient length. Enlarge one end to 12-mm OD and insert a glass wool plug. Attach the other end of the probe to the tee with a short piece of Teflon tubing. Connect a rubber suction bulb to the third leg of the tee.
- d. Place the filter end of the probe at the centroid of the duct or at a point ≥ 1 m from the stack wall and, using the rubber suction bulb, purge the probe completely with stack gases.
- e. Open the stopcock to the grab flask until the pressure in the flask reaches duct pressure. Close off the stopcock, and remove the probe from the duct.
- f. Remove the tee from the flask and tape the stopcocks to prevent leaks during shipment.
- g. Measure the duct temperature and pressure.

3. **Purged Flask Procedure.** Use this procedure or the evacuated flask procedure (section B2) to collect the samples.

- a. Attach one end of the sampling flask to a rubber suction bulb. Attach the other end to a 6-mm OD glass probe as described in step B2c.
- b. Place the filter end of the probe as in step B2d, and use the suction bulb to completely purge the probe and flask.
- c. Close off the stopcock near the suction bulb, and then close off the stopcock near the probe.
- d. Remove the probe from the duct, and disconnect both the probe and suction bulb. Tape the stopcocks to prevent leakage during shipment.
- e. Measure the duct temperature and pressure.

C. Flexible Bags

1. Prepare new bags made of Tedlar or aluminized Mylar. Leak-check them before field use (see FP 3b).
2. Fill the bag with N₂ or air, allow to stand for 24 hr, and analyze the gas by GC at high sensitivity for organics.

Note: The volume of the evacuated bag must be known when doing an in-the-bag dilution of the sample.

3. Collect the samples according to FP 18a.

D. Other Measurements

1. Obtain the moisture content from plant personnel or measure directly, using either psychrometry (<59°C) or Method 4.
2. Obtain the static pressure from the plant personnel or measure it.

E. Final Sampling and Analysis Procedure

Considering safety (flame hazards), source conditions, and pretest survey results, select an appropriate sampling and analysis procedure. The following are some considerations:

1. In situations where a H₂ flame is a hazard and no intrinsically safe GC is suitable, use the flexible bag collection technique or an adsorption technique.

2. Use the direct interface method if the source effluent is <100 °C, the moisture content of the gas does not interfere with the analysis procedure, the physical requirements of the equipment can be met at the site, and the source gas concentration is low enough that detector saturation is not a problem. Adhere to all safety requirements with this method.
3. If the source gases require dilution, use a dilution interface and either the bag sample or adsorption tubes. The choice between these two techniques will depend on the physical layout of the site, the source temperature, and the storage stability of the compounds if collected in the bag.
4. Sample polar compounds by direct interfacing or dilution interfacing to prevent sample loss by adsorption on the bag.
5. Use stainless steel, Pyrex glass, or Teflon materials of construction for sample-exposed surfaces.
6. See subsequent procedures.

FIELD DATA SHEET 18
Gaseous Organic Compounds
Preliminary Site-Survey

I. Client/Plant Name _____ Job # _____
 Address _____ Date _____

 Corporate Contact _____ Phone # _____
 Plant Contact _____ Phone # _____
 Test Location(s) _____

II. Process Description _____

 Raw Material _____

 Products _____
 Operating Cycle: Check: Batch _____ Continuous _____ Cyclic _____
 Timing of batch or cycle: _____
 Best time to test: _____

III. Sampling Site
 A. Site Description _____
 Duct/stack shape and dimensions _____
 Material _____ Wall thickness _____ inches
 Upstream distance to flow disturbance _____ inches _____ diameters
 Downstream distance to flow disturbance _____ inches _____ diameters
 No. of ports available _____ Port inside diameter _____ inches Port nipple length _____ inches
 Size of access area _____
 Hazards _____

Ambient temperature at test location _____ °F

B. Properties of the gas stream
 Temperature Range _____ °F Data source _____
 Velocity _____ ft/sec Data source _____
 Static pressure _____ in. H₂O Data source _____
 Moisture Content _____ % Data source _____
 Particulate Content _____ Data source _____

Gaseous components:

N₂ _____ Hydrocarbons _____ ppm
 O₂ _____
 CO _____
 CO₂ _____

Hydrocarbon components:

_____ ppm
 _____ ppm
 _____ ppm
 _____ ppm

FIELD DATA SHEET 18 (Continued)

C. Sampling consideration

Location to set up GC _____

Special hazards to be considered _____

Power availability at sample location _____

Power availability for GC _____

Plant safety requirements _____

Vehicle traffic rules _____

Plant entry requirements _____

Security agreements _____

Potential Problems _____

D. Site Diagrams. (Attach additional sheets if required).

LABORATORY PROCEDURE 18
GC Analysis Development

A. Selection of GC Parameters

1. Using the pretest survey information, select a column that provides good resolution and rapid analysis time. Consulting column manufacturers is recommended.
2. Using the standards (see CP 18) and selected column, perform initial tests to determine appropriate GC conditions for the compounds of interest.
3. Analyze the audit described in 40 CFR Part 61, Appendix C, Procedure 2, "Procedure for Field Auditing GC Analysis." See LDS 18.
4. Prepare pretest survey samples as follows:
 - a. If the samples were collected on an adsorbent, extract the sample as recommended by the manufacturer for removal of the compounds with a solvent suitable to the type of GC analysis.
 - b. Prepare other samples in an appropriate manner.
 - c. Heat the pretest survey sample to the duct temperature to vaporize any condensed material.
5. Inject the samples into analyzer using the GC conditions determined in step A2. Identify all peaks by comparing the known retention times of calibration standards. Identify any remaining unidentified peaks that have areas >5% of the total using GC/mass spectroscopy (GC/MS), GC/infrared techniques, or estimation of possible compounds by their retention times compared to known compounds, with confirmation by further GC analysis.
 - a. To inject a sample, draw sample through the loop at a constant rate (100 mL/min for 30 sec). Be careful not to pressurize the gas in the loop.

b. Turn off the pump and allow the gas in the sample loop to come to ambient pressure. Activate the sample valve.

c. Determine the GC parameters (see LDS 18).

6. Vary the GC parameters during subsequent injections to determine the optimum settings. After determining the optimum settings, perform repeat injections of the sample to determine the retention time of each compound (must be repeatable to within ± 0.5 sec).
7. If the concentrations are too high for appropriate detector response, use a smaller sample loop or dilutions gas samples and, for liquid samples, dilute with solvent.

B. Preparation of Calibration Curves

1. Establish proper GC conditions.
2. Inject each standard (three per attenuator range) until two consecutive injections give area counts within $\pm 5\%$ of their average. See CP 18 for the preparation of calibration standards.
3. Plot concentrations along the abscissa and the calibration area values along the ordinate. Perform a regression analysis, and draw the least squares line.

C. Relative Response Factor

1. Relate the calibration curve from the cylinder standards for a single organic to the GC response curves of all the compounds in the source by response factors developed in the laboratory.
2. Use this single organic compound to "calibrate" the GC in the field for all compounds measured.

LABORATORY DATA SHEET 18
GC Chromatographic Conditions

Client/Plant Name _____ Job # _____

City /State _____ Date _____

Test Location(s) _____

| <u>Components to be analyzed</u> | <u>Expected concentration</u> |
|----------------------------------|-------------------------------|
| _____ | _____ |
| _____ | _____ |
| _____ | _____ |
| _____ | _____ |
| _____ | _____ |
| _____ | _____ |

Suggested chromatographic column _____

Column flow rate _____ mL/min Head pressure _____ mm Hg

Column temperature: Isothermal _____ °C Programmed from _____ °C to _____ °C at _____ °C/min

Injection port/sample loop temperature _____ °C Detector temperature _____ °C

Detector flow rates: Hydrogen _____ mL/min head pressure _____ mm Hg

Air/Oxygen _____ mL/min head pressure _____ mm Hg

Chart speed _____ inches/minute

Compound data:

| <u>Compound</u> | <u>Retention times</u> | | <u>Attenuation</u> |
|-----------------|------------------------|------------------|--------------------|
| | <u>Inject #1</u> | <u>Inject #2</u> | |
| _____ | _____ / _____ | _____ | |
| _____ | _____ / _____ | _____ | |
| _____ | _____ / _____ | _____ | |
| _____ | _____ / _____ | _____ | |
| _____ | _____ / _____ | _____ | |
| _____ | _____ / _____ | _____ | |
| _____ | _____ / _____ | _____ | |
| _____ | _____ / _____ | _____ | |

_____ Retention times repeatable to $\leq \pm 0.5$ seconds?

CALIBRATION PROCEDURE 18

Calibration Gas Preparation

A. *Calibration Standards*

Using the information from FP 18, prepare or obtain enough calibration standards so that there are at least three different concentrations of each organic compound expected to be measured. Select the concentrations to bracket the stack levels. Mixtures may be used. Use one of the following procedures in the following sections for preparing standards or the respective NIOSH procedures:

B. *Dilution of High Concentration Cylinder Standard*

1. Refer to Figures C18-1 (<1:20 dilution) and C18-2 (>1:20 dilution) or use commercially available dilution systems. Calibrate with diluent gas the rotameters or other flow meters using a bubble meter, spirometer, or wet test meter (see CDS 18a).
2. Leak-check the Tedlar bag according to FP 3b. Set up the system as shown in Figure C18-1 or Figure C18-2.
3. Adjust the gas flow to provide the desired dilution (<1:20 dilution). Fill the bag with sufficient gas for GC calibration. Do not overfill and cause the bag to pressurize. See CDS 18b.
4. Calculate the diluted concentration.

C. *Preparation of Standards from Volatile Materials - Gas Injection Technique*

Use this procedure for organic compounds that exist entirely as a gas at ambient conditions. See CDS 18c.

1. Leak-check the 10-L Tedlar bag according to FP 3b.
2. Evacuate the bag, and meter in 5.0 L of air or N₂ through an appropriate dry gas meter.
3. While the bag is filling, inject with a 0.5-ml syringe a known quantity of the "pure" gas of the organic compound through the wall of the bag or through a septum-capped tee at the bag inlet. Withdraw the syringe needle, and immediately cover the resulting hole with a piece of masking tape.
4. Place each bag on a smooth surface, and alternately depress opposite sides of the bag 50 times to mix the gases.

5. Calculate each organic standard concentration.

D. *Preparation of Standards from Volatile Materials - Liquid Injection Technique*

1. Use the equipment shown in Figure C18-3 and CDS 18c. Calibrate the dry gas meter with a wet test meter or a spirometer. Use a water manometer for the pressure gauge and glass, Teflon, brass, or stainless steel for all connections. Connect a valve to the inlet of the 50-liter Tedlar bag.
2. Assemble the equipment as shown in Figure C18-3, and leak-check the system. Completely evacuate the bag. Fill the bag with hydrocarbon-free air, and evacuate the bag again. Close the inlet valve.
3. Turn on the hot plate, and allow the water to reach boiling. Connect the bag to the impinger outlet. Record the initial meter reading, open the bag inlet valve, and open the cylinder. Adjust the rate so that the bag will be completely filled in about 15 min. Record meter readings.
4. Allow the liquid organic to equilibrate to room temperature. Using a 1.0- or 10- μ L syringe, inject the desired liquid volume into the flowing air stream through the impinger inlet septum. Use a needle of sufficient length to permit injection of the liquid below the air inlet branch of the tee. Remove the syringe.
5. When bag is filled, stop the pump, and close the bag inlet. Record the meter readings.
6. Disconnect the bag from the impinger outlet, and either set it aside for at least 1 hr or massage the bag to ensure complete mixing.
7. Determine the solvent liquid density at room temperature; accurately weigh a known volume (use a ground-glass stoppered 25-ml volumetric flask or a glass-stoppered specific gravity bottle) of the material to ± 1.0 mg. Alternatively, use literature values at 20°C.
8. Calculate each organic standard concentration.

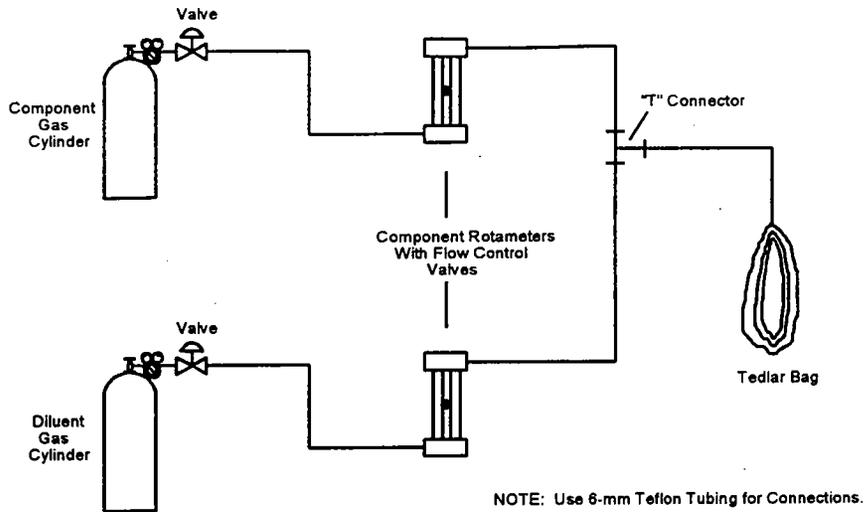


Figure C18-1. Single-Stage Calibration Gas Dilution System.

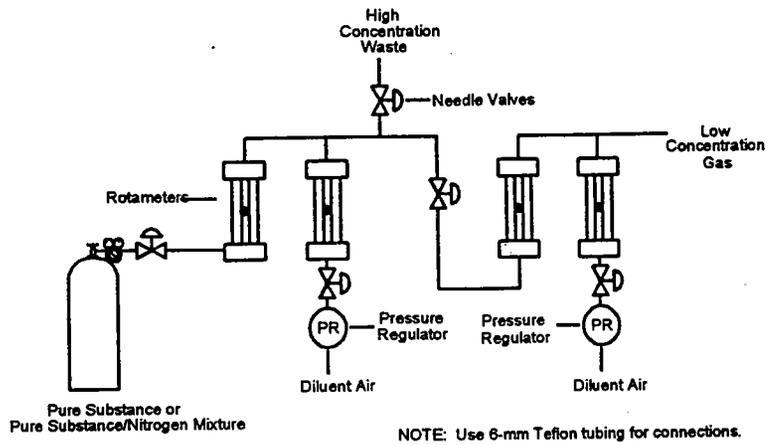


Figure C18-2. Two-Stage Dilution Apparatus.

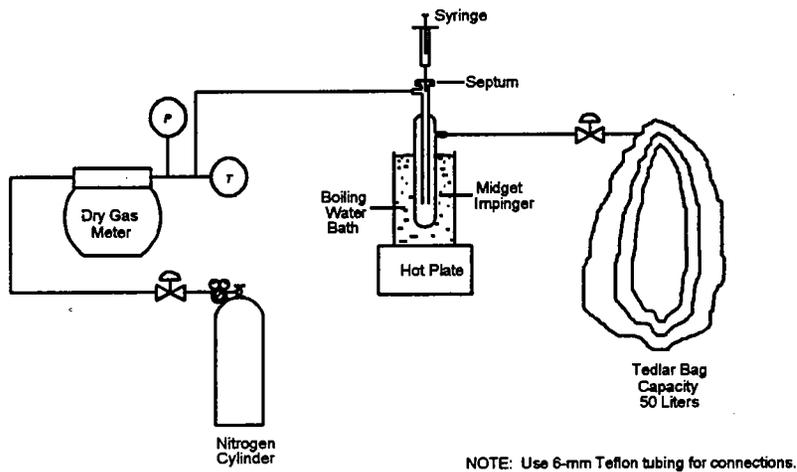


Figure C18-3. Apparatus for Preparation of Liquid Materials.

CALIBRATION DATA SHEET 18a
Flowmeter Calibration

Flowmeter ID _____ Flowmeter type _____ Date _____

Calibration device (✓): Bubble meter _____ Spirometer _____ Wet test meter _____ Lab Temp, T_{lab} _____ K

Lab Barometric Pressure, P_{lab} _____ mm Hg Analyst _____

Note: If a spirometer or bubble meter is used, revise the data sheet. For an example of a bubble meter used as a calibration device, see FP 6a.

| Flowmeter | | |
|------------------------|--------------|-----------------------|
| Reading (as marked) | Temp. (K) | Abs Press. (mm Hg) |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |

| Calibration Device (WTM) | | | | | |
|--------------------------|-------------------|---------------------|-------------------------------------|------------------|------------------------------|
| Time, θ (min) | Vol, V_w (L) | Temp., T_w (K) | Δm (cm H ₂ O) | V_{std} (L) | Flow rate, q_c (mL/min) |
| | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |

$$V_{m(std)} = 0.3858 V_w \frac{P_b}{T_w} \qquad q_c = \frac{V_{m(std)}}{\theta}$$

Plot: Flowmeter readings vs flow rate (q_c) at standard conditions. Attach plot.

Note: If the flowmeter is viscosity dependent, generate calibration curves that cover the operating pressure and temperature ranges of the flowmeter.

Note: The following may be used to calculate flow rate readings for rotameters at standard conditions (Q_{std}), but should be verified before application.

$$Q_{std} = 1.611 Q_{lab} \left(\frac{T_{lab}}{P_{lab}} \right)^{1/2}$$

| | | |
|------------|-------------------------------------|-----------------------------------|
| Flow rate: | Laboratory conditions (Q_{lab}) | Standard conditions (Q_{std}) |
| | _____ | _____ |
| | _____ | _____ |
| | _____ | _____ |
| | _____ | _____ |

QA/QC Check
Completeness _____ Legibility _____ Accuracy _____ Specifications _____ Reasonableness _____

Checked by: _____
Personnel (Signature/Date)
Team Leader (Signature/Date)

CALIBRATION DATA SHEET 18b
Gas Standard Preparation by Dilution of Cylinder Standard

Client/Plant Name _____ Job # _____

City/State _____ Date _____

GC ID # _____ Date Last Calibration _____ Analyst _____

Cylinder Standard: Organic _____ Certified concentration, C_c _____ ppm

| Standards Preparation: | Standard Mixture # | 1 | 2 | 3 |
|--|---|---|---|---|
| Stage 1 | Std gas flowmeter reading | | | |
| | Diluent gas flowmeter reading | | | |
| | Lab temperature (K) | | | |
| | Barometric pressure, (mm Hg) | | | |
| | Std gas flow rate, std cond., q_{c1} (mL/min) | | | |
| | Diluent gas flow rate, std cond., q_{d1} (mL/min) | | | |
| | Calculated concentration, C_s (ppm) | | | |
| Stage 2 (if used) | Std gas flowmeter reading | | | |
| | Diluent gas flowmeter reading | | | |
| | Stage 1 gas flow rate, std cond., q_{c2} (mL/min) | | | |
| | Diluent gas flow rate, std cond., q_{d2} (mL/min) | | | |
| | Calculated concentration, C_s (ppm) | | | |
| GC Operating Conditions: | Sample loop vol., (mL) | | | |
| | Sample loop temp. (°C) | | | |
| | Carrier gas flow rate, (mL/min) | | | |
| | Column temp. Initial, (°C) | | | |
| | Rate Change (°C/min) | | | |
| | Final, (°C) | | | |
| Organic peak identification and calculated concentrations: | Injection time (24-hour clock) | | | |
| | Distance to peak, (cm) | | | |
| | Chart speed (cm/min) | | | |
| | Organic retention time, (min) | | | |
| | Attenuation factor | | | |
| | Peak area, (mm ²) | | | |
| | Peak Area x attenuation factor, (mm ²) | | | |

Plot: Peak area x attenuation factor vs calculated concentration.

$$\text{One-stage: } C_s = C_c \frac{q_{c1}}{q_{c1} + q_{d1}} \quad \text{Two-stage: } C_s = C_c \left(\frac{q_{c1}}{q_{c1} + q_{d1}} \right) \left(\frac{q_{c2}}{q_{c2} + q_{d2}} \right)$$

QA/QC Check

Completeness _____ Legibility _____ Accuracy _____ Specifications _____ Reasonableness _____

Checked by: _____

Personnel (Signature/Date)

Team Leader (Signature/Date)

CALIBRATION DATA SHEET 18c
Gas Standards by Gas/Liquid Injection into Bags

Client/Plant Name _____ Job # _____

City/State _____ Date _____

GC ID # _____ Date Last Calibration _____ Analyst _____

| Standards Preparation: | Standard Mixture # | 1 | 2 | 3 |
|--|--|---|---|---|
| | Organic: | | | |
| | Bag I.D. | | | |
| | DGM Y | | | |
| | Final DGM reading (L) | | | |
| | Initial DGM reading (L) | | | |
| | Metered volume, V _m (L) | | | |
| | Avg DGM temp, T _m (K) | | | |
| | Avg DGM Press, P _g (mm Hg) | | | |
| | Avg Bar pressure, P _b (mm Hg) | | | |
| | Abs DGM press, P _b + P _g (mm Hg) | | | |
| | Abs syringe temp, T _s (K) | | | |
| | Abs syringe press, P _s (mm Hg) | | | |
| | Vol. gas in syringe, G _v (mL) | | | |
| | Density of liquid organic, ρ (g/mL) | | | |
| Vol. liquid in syringe, L _v (μL) | | | | |
| GC Operating Conditions: | Sample loop vol. (mL) | | | |
| | Sample loop temp. (°C) | | | |
| | Carrier gas flow rate (mL/min) | | | |
| | Column temp. Initial, (°C) | | | |
| | Rate Change (°C/min) | | | |
| Final, (°C) | | | | |
| Organic peak identification and calculated concentrations: | Injection time (24-hour clock) | | | |
| | Distance to peak (cm) | | | |
| | Chart speed (cm/min) | | | |
| | Organic retention time (min) | | | |
| | Attenuation factor | | | |
| | Peak height (mm) | | | |
| | Peak area (mm ²) | | | |
| | Peak area x attenuation factor (mm ²) | | | |
| Calculated conc., C _s (ppm) | | | | |

Plot: Peak area x attenuation factor vs calculated concentration.

Gas-injection: $C_s = 10^3 \frac{G_v P_s T_m}{V_m Y P_m T_s}$ Liquid-injection: $C_s = 6.24 \times 10^4 \frac{L_v \rho T_m}{m V_m Y P_m}$

QA/QC Check

Completeness _____ Legibility _____ Accuracy _____ Specifications _____ Reasonableness _____

Checked by: _____
 Personnel (Signature/Date) _____ Team Leader (Signature/Date) _____

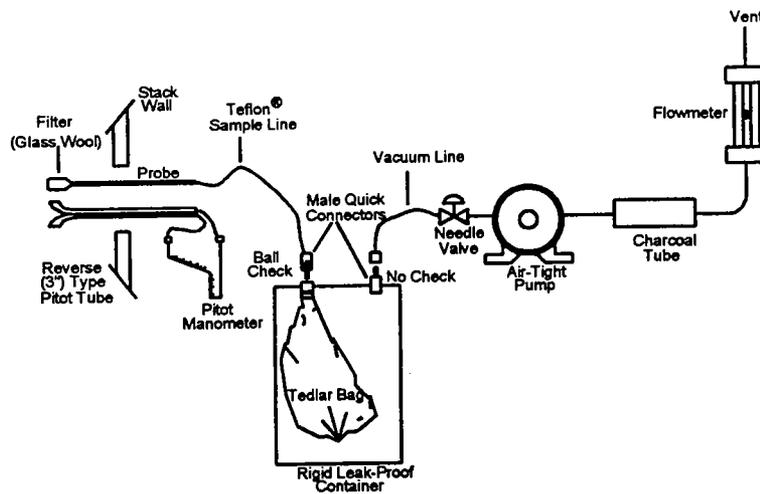


Figure F18a-1. Integrated Bag Sampling Train.

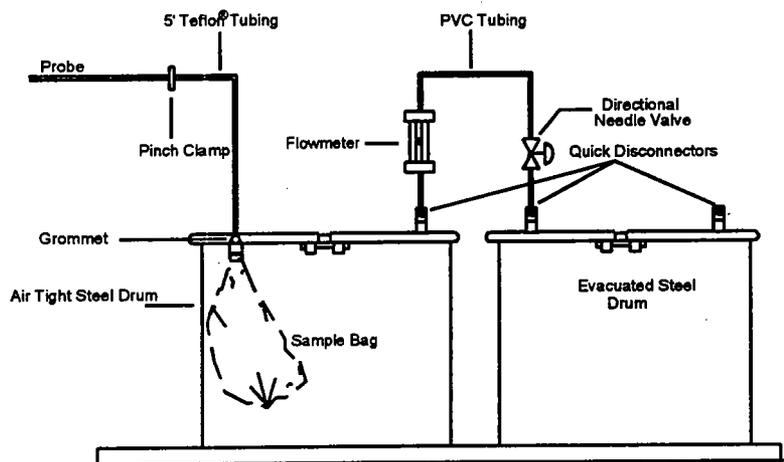


Figure F18a-2. Explosion Risk Gas Sampling Method.

FIELD PROCEDURE 18a
Integrated Bag Sampling

A. Evacuated Container Procedure

Refer to the sample train shown in Figure F18a-1 and FDS 18a. Collect triplicate samples from each sample location.

1. Leak-check both the bags and the container as follows:
 - a. Connect a water manometer using a tee connector between the bag or rigid container and a pressure source.
 - b. Pressurize the bag or container to 2 to 4 in. H₂O, and allow it to stand overnight. A deflated bag indicates a leak.
2. Purge the probe as follows: Connect the vacuum line from the needle valve to the Teflon sample line from the probe. Place the probe inlet at the centroid of the stack, or at a point ≥ 1 m from the stack wall, and purge at 0.5 L/min for sufficient time to purge the line several times.
3. Evacuate the bag as follows: Connect the vacuum line to the bag, and evacuate until the rotameter indicates no flow.
4. Reconfigure the sample and vacuum lines for sampling, and sample proportional to the stack velocity. As a precaution, direct the gas exiting the rotameter away from sampling personnel.
5. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Record the information shown in FDS 18a.
6. Protect the Tedlar bag and its container from sunlight. When possible, perform the analysis within 2 hr of sample collection. See LP 18a.
7. After analysis, leak-check both the bags and the container as in step 1.

B. Direct Pump Procedure

Follow section A, except for the following variations:

1. Place the pump and needle valve between the probe and the bag.
2. Leak-check the system, and then purge with stack gas before connecting to the previously evacuated bag.

C. Explosion Risk Area Bag Sampling Procedure

Use this method whenever there is a possibility of an explosion due to pumps, heated probes, or other flame producing equipment. Follow step A, except replace the pump with another evacuated container (see Figure F18a-2).

D. Other Modified Bag Sampling Procedures

If condensation occurs in the bag during sample collection and a direct interface system cannot be used, use either of the following modifications:

1. Heating. Heat (conforming to safety restrictions) the box containing the sample bag to the source temperature (assuming system can withstand this temperature). Maintain the temperature until analysis.
2. Dilution. Leak-check the system (leaky systems may create a potentially explosive atmosphere). Using the setup shown in Figure C18-3 (without midjet impinger section), meter an inert gas into the Tedlar bag. Take the partly filled bag to the source, and meter the source gas into the bag through heated sampling lines and a heated flowmeter, or Teflon positive displacement pump. As a quality control check, dilute and analyze a gas of known concentration and validate technique by checking the dilution factor.

FIELD DATA SHEET 18a
Integrated Bag Sampling

Client/Plant Name _____ Job # _____

City/State _____ Date _____

Test Location/Run # _____ Personnel _____

| Sample No. | 1 | 2 | 3 |
|--|---|---|---|
| Source temperature (°C) | | | |
| Probe temperature (°C) | | | |
| Source pressure, P_g (mm Hg) | | | |
| Barometric pressure, P_b (mm Hg) | | | |
| Abs source pressure ($P_b + P_g$), P_s (mm Hg) | | | |
| Ambient temperature (°C) | | | |
| Sample flow rate (approx) (L/min) | | | |
| Bag No. | | | |
| Start time | | | |
| Finish time | | | |

QA/QC Check

Completeness _____ Legibility _____ Accuracy _____ Specifications _____ Reasonableness _____

Checked by: _____
 Personnel (Signature/Date) Team Leader (Signature/Date)

LABORATORY PROCEDURE 18a
Integrated Bag Sample Analysis**A. Analysis**

1. Connect the needle valve, pump, charcoal tube, and flowmeter to draw gas samples through the gas sampling valve.
2. Flush the sample loop with gas from one of the three Tedlar bags containing a calibration mixture, and analyze the sample.
3. Obtain at least two chromatograms for the sample or until the peak areas from two consecutive injections agree to within $\pm 5\%$ of their average.
4. After obtaining acceptable results, analyze the other two calibration gas mixtures in the same manner.
5. Prepare the calibration curve by using the least squares method.
6. Analyze the two field audit samples by connecting each Tedlar bag containing an audit gas mixture to the sampling valve. Calculate the results; report the data to the audit supervisor. If the results are acceptable, proceed with the analysis of the source samples.
7. Analyze the source gas samples by connecting each of the three bag samples to the sampling valve with a piece of Teflon tubing identified with that bag. Follow the restrictions on replicate samples specified for the calibration gases (step A3).
8. After all three bag samples have been analyzed, repeat the analysis of the calibration gas mixtures. Use the average of the two calibration curves to determine the respective sample concentrations. If the two calibration curves differ by $> 5\%$ from their mean value, then report the final results by both calibration curves.

B. Recovery Study

1. Prepare (if not already available) calibration gas mixtures of all target compounds within 40 to 60% of the average concentration of the three bag samples. If not detected, use a concentration 5 times the detection limit of that compound.

2. Select one of the three bag samples and analyze in duplicate as in step A3. Then spike the bag sample with calibration gas mixtures of all the target pollutants.
3. Analyze the bag sample three times after spiking and average the results.
4. Calculate the recovery, R, for each target compound (must be $0.70 \leq R \leq 1.30$).
5. Adjust field sample concentrations using R for each compound.

C. Determination of Bag Water Vapor Content

1. Measure the ambient temperature and barometric pressure near the bag.
2. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a decimal figure. Assume the relative humidity to be 100% unless a lesser value is known.

D. Notes

1. Eliminate resolution interferences by selecting appropriate GC column and detector or by shifting the retention times through changes in the column flow rate and the use of temperature programming.
2. Periodically analyze blanks that consist of hydrocarbon-free air or N_2 to demonstrate that analytical system is essentially free from contaminants.
3. To eliminate sample cross-contamination that occurs when high-level and low-level samples or standards are analyzed alternately, thoroughly purge the GC sample loop between samples.
4. To assure consistent detector response, prepare calibration gases in dry air.

LABORATORY DATA SHEET 18a
GC Analysis of Field Samples

Client/Plant Name _____ Job # _____

City/State _____ Date _____

Sample Moisture Content, B_{ws} _____ Personnel _____

Note: Conduct a pre- and post-test calibration using three gas mixtures from CDS 18b or c, plot calibration curve, and attach. Record the average barometric pressure and temperature of the pre- and post-test conditions here:

P_r _____ mm Hg T_r _____ K *Note: Use more data sheets as needed.*

Chromatograph Operation

| Parameter | Setting | Parameter | Setting |
|-----------------------------------|---------|---------------------------------|---------|
| Sample loop volume (mL) | | Detector temp (°C) | |
| Sample loop temp, T_i (K) | | Chart speed (cm/min) | |
| Column temp initial (°C) | | Sample flow rate (mL/min) | |
| Column temp. program rate (°C/mL) | | Dilution gas flow rate (mL/min) | |
| Column temp final (°C) | | Dilution Gas used (symbol) | |
| Carrier gas flow rate (mL/min) | | Dilution ratio, D_f | |

Bar. pressure during sample analysis, P_i _____ mm Hg

Samples to be analyzed in addition to field samples: Two Audits, Blanks, Spiked and Unspiked Field Sample

| Sample ID | Inject'n Time (Clock) | Organic Compnt | Dist to Peak (cm) | Retent. Time (sec) | Atten. Factor A_c | Peak Area, A_{m2} (mm ²) | $A_c \times A_{m2}$ (mm ²) | Conc. C_s (ppm) | Calc Cor C_c (ppm) |
|-----------|-----------------------|----------------|-------------------|--------------------|---------------------|--|--|-------------------|----------------------|
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_____ The pre- and post- calibration curves are within 5% of their mean value? If not, report final results by comparison to both calibration curves.

_____ Audit analyses agree ± 10% of the audit concentrations?

_____ Peak areas from 2 consecutive injections agree ± 5% of their average?

$$C_c = \frac{C_s P_r T_i F_r}{P_i T_r (1 - B_{ws})}$$

F_r = Response factor, if needed.

QA/QC Check

Completeness _____ Legibility _____ Accuracy _____ Specifications _____ Reasonableness _____

Checked by: _____ Personnel (Signature/Date) _____ Team Leader (Signature/Date)

FIELD PROCEDURE 18b
Direct Interface Sampling and Analysis

1. Assemble the sampling system as shown in Figure F18b-1. Prepare the GC accordingly. Ensure all connections are tight.
2. Turn on the probe and sample line heaters to achieve a 0 to 3°C above the source temperature.
3. While the probe and sample line are being heated, disconnect the sample line from the gas sampling valve, and attach the line from the calibration gas mixture. Flush the sample loop with calibration gas and analyze a portion of that gas. Calibrate the system with other concentration levels.
4. After successfully calibrating the system, turn the gas sampling valve to flush position, then reconnect the probe sample line to the valve. Attach the mid-level calibration gas for at least one target compound to the inlet of the probe or as close as possible to the inlet of the probe, but before the filter.
5. Analyze the mid-level calibration gas until two consecutive samples are within $\pm 5\%$ of their mean value (this value must be within $\pm 10\%$ of the value obtained in step 3).
6. Analyze two field audit samples, if applicable, through the gas sampling valve at the same instrument conditions as that for the source samples.
7. Reconfigure the train for sampling. Move the probe to the sampling position, and draw source gas into the probe, heated line, and sample loop.
8. After thorough flushing, analyze the sample in duplicate using the same conditions (especially the same pressure) as that for the calibration gas mixture until the duplicates agree within $\pm 5\%$ of their mean value.
9. Remove the probe from the source and analyze a second calibration gas mixture.
10. Record all data on FDS 18b.

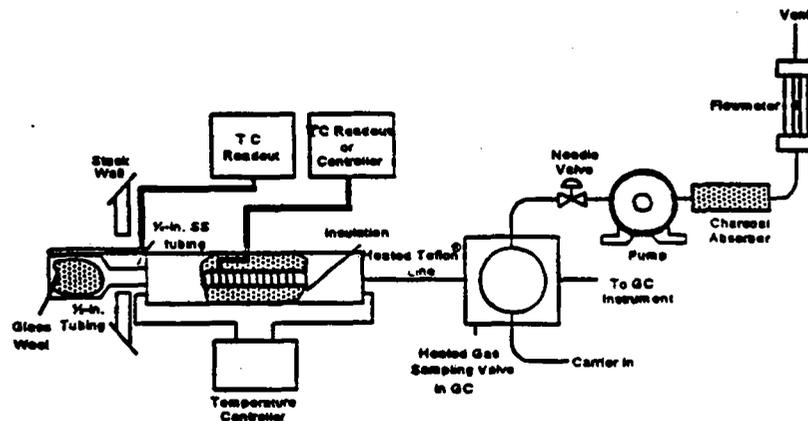


Figure F18b-1. Direct Interface Sampling System.

FIELD DATA SHEET 18b
GC Direct Interface Analysis

Client/Plant Name _____ Job # _____

City/State _____ Date _____

Sample Moisture Content, B_{ws} _____ Personnel _____

Note: Conduct a pre- and post-test calibration using three gas mixtures from CDS 18b or c, plot calibration curve, and attach. Record the average barometric pressure and temperature of the pre- and post-test conditions here:

P_r _____ mm Hg T_r _____ K *Note: Use more data sheets as needed.*

Chromatograph Operation

| Parameter | Setting | Parameter | Setting |
|-----------------------------------|---------|---------------------------|---------|
| Sample loop volume (mL) | | Detector temp (°C) | |
| Sample loop temp, T_i (K) | | Chart speed (cm/min) | |
| Column temp initial (°C) | | Sample flow rate (mL/min) | |
| Column temp. program rate (°C/mL) | | | |
| Column temp final (°C) | | | |
| Carrier gas flow rate (mL/min) | | | |

Bar. pressure during sample analysis, P_i _____ mm Hg Probe/sampling line set at 0-3°C above stack temperature?

Samples to be analyzed in addition to field samples: Two Audits, Mid-Cal Mixture from the inlet to the probe or as close as possible, but before the filter. (Concentration from probe and from analyzer must be within 10%.)

| Sample ID | Inject'n Time (Clock) | Organic Compnt | Dist to Peak (cm) | Retent. Time (sec) | Atten. Factor A_c | Peak Area, A_m (mm ²) | $A_c \times A_m$ (mm ²) | Conc. C_s (ppm) | Calc Conc C_c (ppm) |
|-----------|-----------------------|----------------|-------------------|--------------------|---------------------|-------------------------------------|-------------------------------------|-------------------|-----------------------|
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_____ The pre- and post- calibration curves are within 5% of their mean value? If not, report final results by comparison to both calibration curves.

_____ Peak areas from 2 consecutive injections agree ± 5% of their average?

_____ Audit analyses agree ± 10% of the audit concentrations?

_____ Concentration from probe and from analyzer within ± 10%?

$$C_c = \frac{C_s P_r T_i F_r}{P_i T_r (1 - B_{ws})}$$

F_r = Response factor, if needed.

QA/QC Check

Completeness _____ Legibility _____ Accuracy _____ Specifications _____ Reasonableness _____

Checked by: _____

Personnel (Signature/Date)

Team Leader (Signature/Date)

FIELD PROCEDURE 18c
Dilution Interface Sampling and Analysis

Note: The apparatus required for this direct interface procedure is basically the same as that described in FP 18b, except a dilution system is added between the heated sample line and the gas sampling valve. The apparatus is arranged so that either a 10:1 or 100:1 dilution of the source gas can be directed to the chromatograph. A pump of larger capacity is also required, and this pump must be heated and placed in the system between the sample line and the dilution apparatus. Use FDS 18c.

1. Assemble the apparatus by connecting the heated box, shown in Figure F18c-1, between the heated sample line from the probe and the gas sampling valve on the chromatograph. Leak-check the system prior to the dilutions so as not to create a potentially explosive atmosphere.
2. Vent the source gas from the gas sampling valve directly to the charcoal filter (eliminate the pump and rotameter). Heat the sample probe, sample line, and heated box. Insert the probe and source thermocouple at the centroid of the duct.
3. Measure the source temperature, and adjust all heating units to 0 to 3°C above this temperature. If this temperature is above the safe operating temperature of the Teflon components, adjust the heating to maintain a temperature high enough to prevent condensation of water and organic compounds.
4. Analyze a high concentration calibration gas (one of the target compounds) of known composition through the probe inlet (or as close as possible to the inlet) at either the 10:1 or 100:1 dilution stages, as appropriate (if necessary, vary the flow of the diluent gas to obtain other dilution ratios) to verify the operation of the dilution system and integrity of sampling system.
5. Analyze the calibration gas until two consecutive samples are within $\pm 5\%$ of their mean value. Determine the concentration of the diluted calibration gas using the dilution factor and the calibration curves prepared in the laboratory (must be within $\pm 10\%$ of the expected values).
6. Verify the GC operation using a low concentration standard by diverting the gas into the sample loop and bypassing the dilution system.
7. Analyze two field audit samples using either the dilution system, or directly connect to the gas sampling valve as required.
8. After the dilution system and GC operations are satisfactory, analyze the source gas in duplicate until two consecutive values are within $\pm 5\%$ of their mean.
9. Analyze again the calibration gas mixtures.

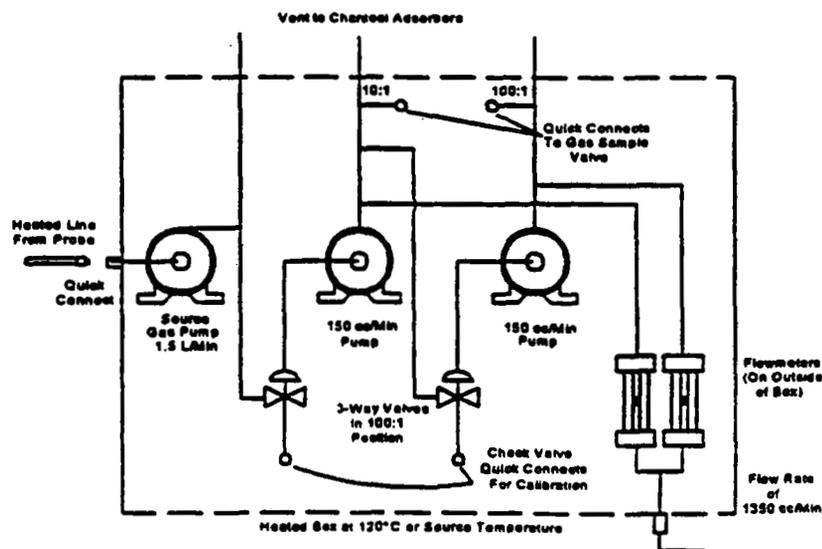


Figure F18c-1. Schematic Diagram of the Heated Box Required

FIELD DATA SHEET 18c
GC Dilution Interface Analysis

Client/Plant Name _____ Job # _____

City/State _____ Date _____

Sample Moisture Content, B_{ws} _____ Personnel _____

Note: Conduct a pre- and post-test calibration using three gas mixtures from CDS 18b or c, plot calibration curve, and attach. Record the average barometric pressure and temperature of the pre- and post-test conditions here:

P_r _____ mm Hg T_r _____ K *Note: Use more data sheets as needed.*

Chromatograph Operation

| Parameter | Setting | Parameter | Setting |
|-----------------------------------|---------|---------------------------------|---------|
| Sample loop volume (mL) | | Detector temp (°C) | |
| Sample loop temp, T_i (K) | | Chart speed (cm/min) | |
| Column temp initial (°C) | | Sample flow rate (mL/min) | |
| Column temp. program rate (°C/mL) | | Dilution gas flow rate (mL/min) | |
| Column temp final (°C) | | Dilution Gas used (symbol) | |
| Carrier gas flow rate (mL/min) | | Dilution ratio, D_f | |

Bar. pressure during sample analysis, P_i _____ mm Hg Probe/sample line set at 0-3°C above stack temperature?

Samples to be analyzed in addition to field samples: Two Audits, High-Cal Mixture from the inlet to the probe or as close as possible, but before the filter, and through the appropriate dilution system (Concentration determined must be within ± 10% of expected value.)

| Sample ID | Inject'n Time (Clock) | Organic Compnt | Dist to Peak (cm) | Retent. Time (sec) | Atten. Factor A_c | Peak Area, A_{m_p} (mm ²) | $A_c \times A_{m_p}$ (mm ²) | Conc. C_s (ppm) | Calc Conc C_c (ppm) |
|-----------|-----------------------|----------------|-------------------|--------------------|---------------------|---|---|-------------------|-----------------------|
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_____ The pre- and post- calibration curves are within 5% of their mean value? If not, report final results by comparison to both calibration curves.

_____ Peak areas from 2 consecutive injections agree ± 5% of their average?

_____ Audit analyses agree ± 10% of the audit concentrations?

_____ Concentration of High-Cal gas within ± 10% of expected value?

$$C_c = \frac{C_s P_r T_i F_r D_f}{P_i T_r (1 - B_{ws})}$$

F_r = Response factor, if needed.

QA/QC Check

Completeness _____ Legibility _____ Accuracy _____ Specifications _____ Reasonableness _____

Checked by: _____ Personnel (Signature/Date) Team Leader (Signature/Date)

FIELD PROCEDURE 18d
Adsorption Tube Sampling and Analysis

Note: Refer to the National Institute for Occupational Safety and Health (NIOSH) method for the particular organics to be sampled. The principal interferant is water vapor. Above 3% water vapor (see FDS 18), use silica gel before the charcoal. When more than one compound is present in the emissions, develop relative adsorptive capacity information. Analyze the samples according to LP 18a (use LDS 18a).

A. Sampling

1. After the normal clean up, clean the probe with extraction solvent. Although borosilicate glass or stainless steel probes are acceptable, use Teflon probes and connecting lines as much as possible.
2. Assemble the sampling system as shown in Figure F18d-1. Mount the adsorption tubes in a vertical direction to prevent channeling during sampling. Use minimal length of flexible tubing between the probe and adsorption tubes.
3. Calibrate the sampling system (pump, limiting orifice, adsorption tubes, probe, etc.) with the bubble tube flowmeter. Use FDS 6a.
4. Place the probe at the centroid or at a point ≥ 1 m from the stack wall. Sample at a constant rate, using the rotameter as an indicator.
5. Obtain a total sample volume commensurate with the expected concentration(s) of the volatile organic(s) present, and recommended sample loading factors (weight sample per weight adsorption media). Record the information shown in FDS 6a.
6. Towards the end of the test run, use the bubble-tube flowmeter to measure the flow rate through the sampling train.
 - a. If the final flow rate is $\leq 5\%$ of initial flow rate, use the initial flow rate to calculate the sample volume.
 - b. If the final flow rate is $> 5\%$ but $\leq 20\%$ of initial, use the average of the two to calculate sample volume.
7. Leak-check the pump and volume flow rate immediately after sampling with all sampling train components in place. See FP 3c, sections C and D.
8. Remove adsorption tubes and cap tightly. Label tubes.
9. Rinse the probe and sampling lines up to the adsorption tube with desorption solvent. Store in glass bottles, and refrigerate (if necessary). Seal and label the bottle.

B. Recovery Study

Obtain triplicate samples.

1. Set up two identical sampling trains. Designate one train as "S" for spiked, and the other as "U" for unspiked.
2. Spike all the compounds of interest (in gaseous or liquid form) unto the adsorbent tube(s) in the spiked train before sampling (about 40 to 60% of mass expected from stack samples).
3. Collocate the probes in the stack of the duplicate trains. Position the probe nozzles on the same plane, 2.5 cm apart with pitot tubes on the outside of each probe.
4. Sample as in step A.
5. Analyze the samples along with the other field samples and determine the fraction of spiked compound recovered for each compound. Determine the average (R) of all three runs (must be $0.70 \leq R \leq 1.30$).
6. Adjust field sample concentrations using R for each compound.

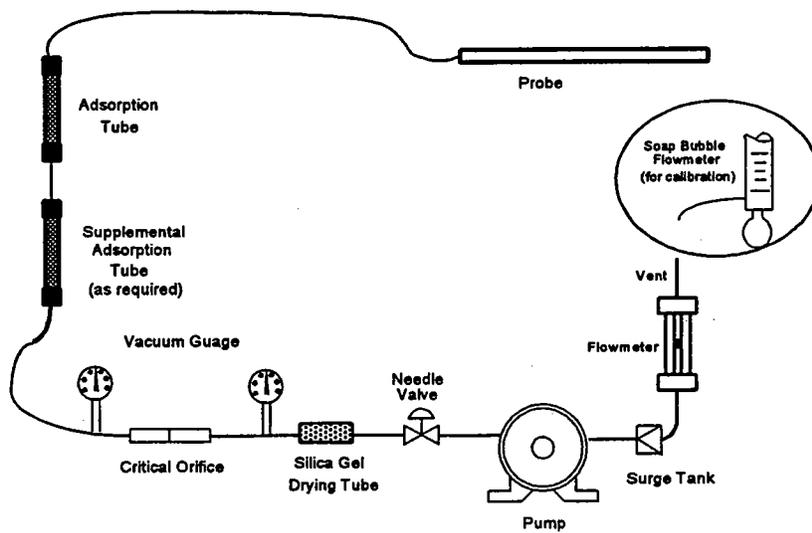


Figure F18d-1. Adsorption Tube Sampling System.

